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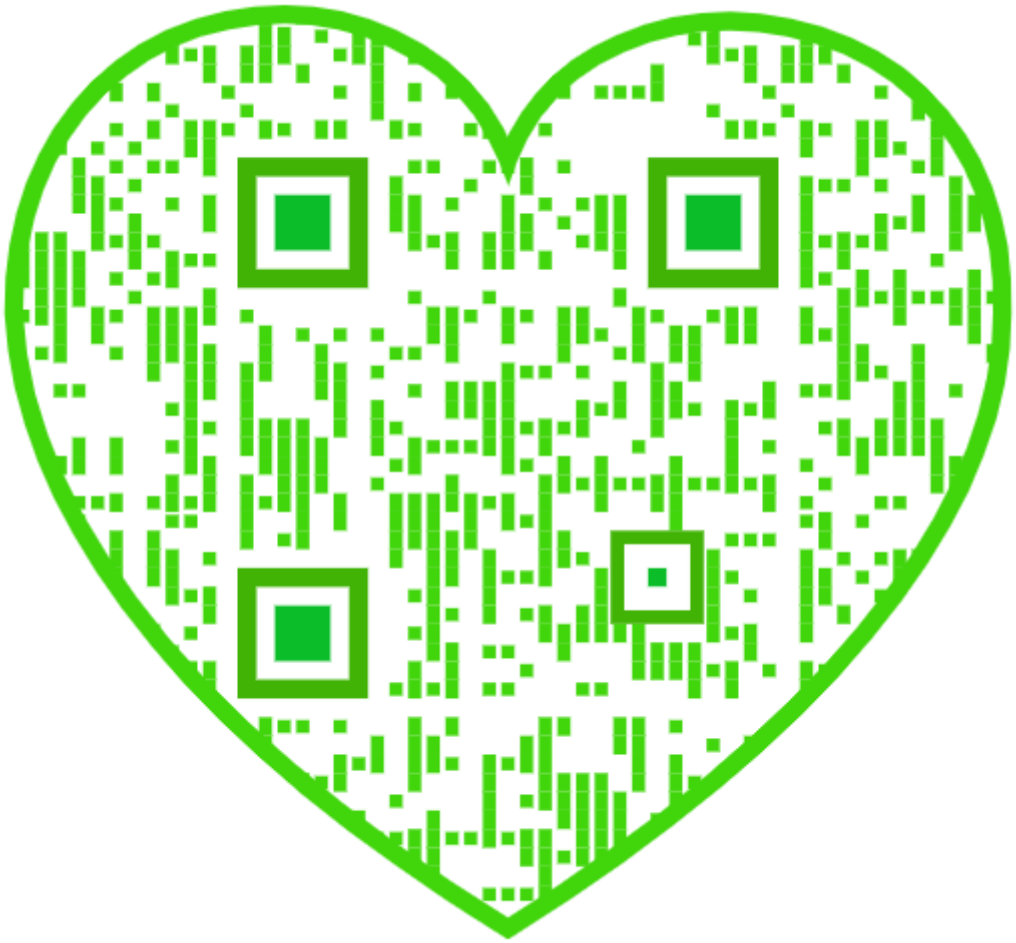

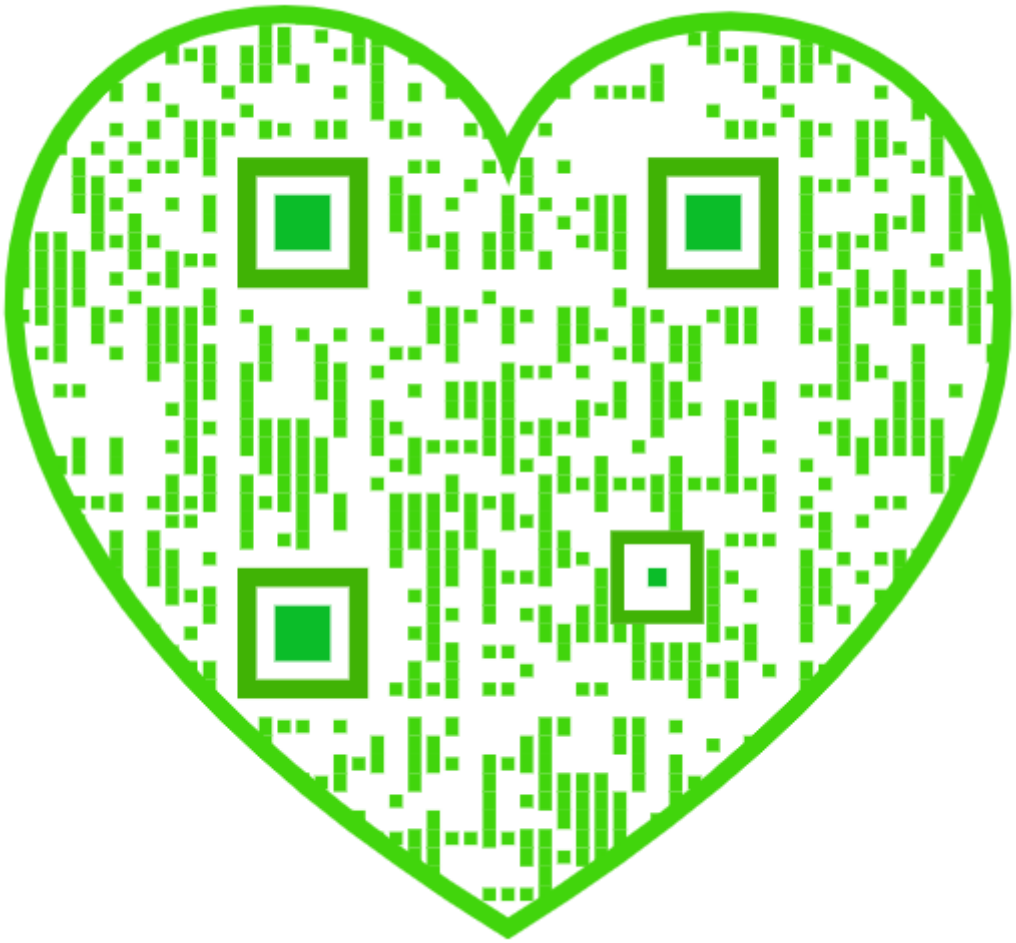

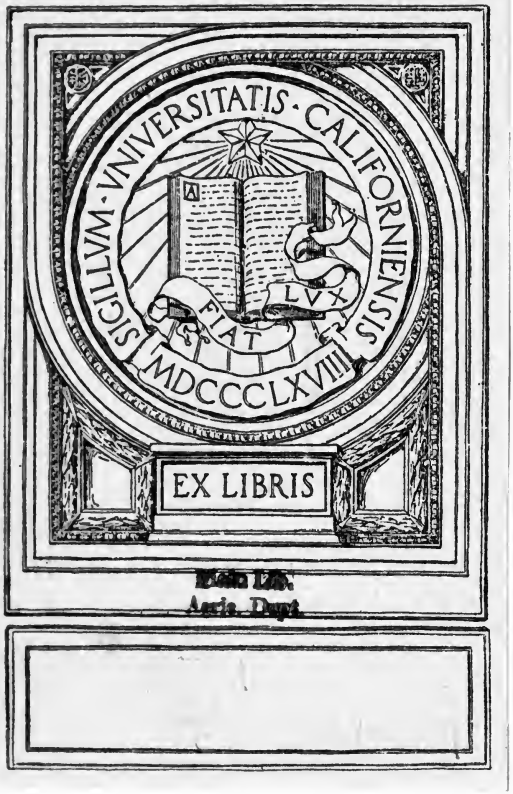

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THE USEFUL PROPERTIES OF CLAYS.

INTRODUCTION.

From the earliest dawn of history man has exercised himself in fashioning into products of beauty and utility the plastic materials which he found prepared for his hand on or under the surface of the earth. The stone age was followed by the bronze, and this in time by that of iron, and this in turn by the age of steam and electricity; but throughout all these changes the plastic arts have flourished in proportion to the height of civilization that the peoples have reached. Science and art, poetry and history combine to lend fascination to a study of clays and clay working. Records of the manners and customs of old and almost forgotten civilizations, such as the Mycenæan, or the Mexican, are carefully gleaned by the archæologist from the more or less crude linear markings and figures depicted on fragments of pottery and statuary which have come down to us. From the few rude earthenware chips which remain to tell us of our prehistoric ancestors to the finished and delicate porcelains of Dresden and Sèvres, the industry of man records its own development.

Although in the direction of pure utility, as in the manufacture of bricks, tiles, and common earthenware, much has been accomplished, the fact is before us that, in the production of works of art and beauty fashioned from clay, America is not to-day the equal of Europe. The reasons for this are various and need not be discussed here. It is sufficient to point out that they are not of such a nature as to prevent America from ultimately achieving the highest position of all in this domain. The fact that many tons of clay of various sorts are annually brought across the ocean to us for use in our potteries, might seem to indicate that our native clays were of themselves unfit for use. If indeed this were true, it would be an insuperable obstacle to final success, but the fact is that, although it may at present be more profitable to import a clay than to develop a native source, America undoubtedly possesses unusually rich clay and kaolin deposits, some of which are fitted for the production of the most delicate and beautiful objects. It is interesting to note that the pottery which has been a pioneer in works of art made entirely of native clays was founded and fostered by an American woman. It is by just such efforts that wider and further growth will come. In these days of ardent emulation and competition among the nations, it is fair to anticipate the time when an American

name shall be added to those which stand for the highest achievement in ceramics, or the art of clay working. As soon as a greater number of individuals among our people become interested in the properties and possibilities of our native clay bodies, development is sure to follow. Clay working is neither so difficult nor so expensive but that in some cases objects of art have been molded in the home and burnt in private kilns. On the other hand success is attained only at the price of diligent study and persistent effort. It is with the hope that the dissemination of knowledge concerning the useful properties of clay will lead to a wider popular interest in their study and use, that this article is written.

FORMATION OF CLAYS.

Clay may be defined as an earthy deposit, found on or below the surface, which when finely ground and mixed with water forms a moldable or plastic mass and can be burned to a hard, stonelike substance after drying. The original crust of the earth was of course formed of the rocks which crystallized from a molten magma. These crystalline rocks of igneous origin underwent gradual crumbling and decay caused by the varied actions of the elements. It is probable that only students of rock structure realize how steadily and continually rocks are undergoing secondary changes and decay. "Enduring as the rocks" is an expression of merely relative truth. When rocks crumble the resulting material may be found either heaped up in place, in which case they are known as residual deposits, or the fine material may have been picked up in suspension by moving waters, sifted out and deposited at some remote place in beds or layers forming sedimentary deposits. These deposits once formed have been, in some cases, acted on by tremendous forces in the course of the great geologic periods. Folded and buried under great crumplings of the earth's crust they have been to varying degrees subjected to heat and pressure and have thus become metamorphosed. Consolidated into sedimentary rocks and shales they become again subject to decay. Changed and disintegrated, now acted on by percolating waters, in which it is known that many of these crystalline minerals are distinctly soluble, or again subjected to acid or alkaline solutions, as the case may be, it is little wonder that every useful earthy deposit found by man on the surface of the earth is to a certain degree unique in its properties, requiring special study and treatment in order to insure the highest degree of success in its working. Clays of nearly the same chemical composition and of similar physical texture, owing to some slight modification will yield entirely dissimilar results in mixing, molding, and firing. Given in some particular locality a deposit which under certain treatment yields a definite and constant result to man's handicraft, it is doubtful whether, if the deposit becomes exhausted, exactly similar results could be pro-

duced elsewhere even by the selfsame artisans. It is to some extent owing to these reasons that the great potteries of the world maintain their distinctive styles, and also lose them as in the cases where the finest modern examples are inferior to the older work. The loss of the art of the ancients, renowned for their pottery and glazes, is possibly due to this cause more than to the inability of modern science and industry to duplicate their cunning in artifice. For the reasons outlined we find our clays with all shades of variation in their useful properties.

PRODUCTION AND IMPORTATION OF CLAYS.

The following figures taken from the statistics of the mineral resources of the United States, compiled by the U. S. Geological Survey for the year 1902, show in an interesting way the condition of our clay-producing industry: Total imports of clays, 168,551 long tons, valuation $1,154,-805; total domestic production of clays, 1,299,426 long tons, valuation, $2,061,072.

Altogether the total amount of clays imported into this country is between one-seventh and one-eighth of that produced here, while the valuation of the latter is less than twice that of the former. Doubtless in time the rich clay deposits of America will be developed to a point where this considerable importation of expensive clays will cease, and one of the factors in this progress will be a better understanding of the useful qualities of clays.

KINDS OF CLAY.

With few exceptions residual clays, or those derived from the decomposition of rocks in place, are fit only for the commoner grades of brick and earthenware. Nearly all the smoother and finer textured clays are formed from the sedimentary plastic products of rock decay. These beds may be, however, of a widely different nature, some being sandy, or to use a technical expression, "lean," and others very fine-grained, plastic, and "fat." By the accumulation of beds of fine-grained material, one on top of another, the clays become consolidated into shales. These shales which are much used in certain localities are sometimes as hard as rock, but when ground and mixed with water yield a plastic, workable mass. In actual pottery practice it is usual to mix several different kinds of clays, thus combining the useful qualities of each. Probably more than 90 per cent of all manufactured articles are molded of a mixture of at least three clays.

The various sorts of clays have come to be distinguished by different names; thus one hears of stone-ware, china, and brick clays; pipe clays, ball clays, fire clays, and kaolins. These distinctions are not very exact, and in most cases merely show the local use to which the clay is put. China clays are usually white or burn white, and, when mixed with ball clay, ground feldspar, and quartz, are used in the manufacture of por-

celain and other forms of white ware. Ball clay is the name given to very fat plastic clays which can be formed and molded into shape and which will dry out to a mass of high binding power without suffering deformation. Used by themselves ball clays will rarely stand the fire well, but for mixing with good burning clays of low binding power and little or no plasticity they are very necessary. Florida supplies these clays to a considerable extent, but for special reasons they are at present very largely imported from England and Germany. Kaolins are made up of fine particles of the mineral kaolinite which results from the decomposition of feldspar. Kaolin, which, chemically speaking, is a silicate of aluminum, is supposed to be the essential ingredient in all clays, and it is not uncommon to read in various publications that kaolin furnishes the active clay base in all plastic clay. Recent researches made in the Division of Tests of the Bureau of Chemistry, however, show that such statements do not express the whole truth of the matter. Fire clays, as their name signifies, are those which do not fuse or melt except at very high temperatures, 3,500° F. and over; although these clays are generally used in the manufacture of fire bricks, muffles, and linings for furnaces, they can be used for decorative purposes, as their very stability in the fire makes them easy to burn.

PHYSICAL PROPERTIES OF CLAY.

We may now turn to the consideration of the physical properties of clay, taking them in the following order: (1) Plasticity; (2) binding power (tensile strength); (3) slaking; (4) air shrinkage; (5) firing qualities—(a) fire shrinkage (distortion), (b) fusibility, (c) color; (6) absorptiveness.

PLASTICITY.

It is a matter of common observation that the particles of all wet powders to a greater or a less degree cohere. If we take ordinary clean, white, sea sand, grind it to an impalpable powder and mix it with a certain amount of water, we shall have a mass just sufficiently coherent to ball together. If, however, we try to mold the wet mass into a form it quickly crumbles and shows itself quite unworkable. From this extreme up to the most plastic of the ball clays which will respond to every touch of the artist's hand and preserve every line of the graver's tool, we find among the fine-grained materials on the earth's surface every grade of variation.

The cause of this wonderful property has been much discussed by students of clay structure. Investigations carried on in the Division of Tests show that the effect is due to the presence of a certain proportion of particles which actually soften and become sticky under the action of water. It has been noted that purely crystalline particles do not make plastic masses, but there is another kind of matter than that which

appears in a crystalline form. This is broadly defined as amorphous substance. Only one kind of amorphous matter, however, is active in producing plasticity. Glass is an amorphous, noncrystalline material, but powdered glass is no more plastic when wet than is sand. The particles which are active in forming coherent masses are highly hydrated, that is, they contain so-called water of combination, which disappears into some sort of porous structure too fine to be seen even under the most powerful microscope. Clays, even when thoroughly dried in the sun and air so that they have every appearance of being dry powders, will sometimes contain as much as 12 or 14 per cent of this combined water. If the clay is heated to a sufficiently high temperature to drive off this water all plasticity and clay likeness is gone. Thus brick dust is no more plastic than sand or glass-powder. The particles have not become crystalline by heating, but the active hydrated particles have been changed into dead amorphous ones. These active particles which become coherent when wet are called *colloid* (which means glue-like), to distinguish them from the inactive crystalline and amorphous grains which are also present in almost every clay.

BINDING POWER.

It is this property which provides strength in the air-dried clay so that articles fashioned of it can be transported to the kiln without crumbling and breaking. It is a very important quality and the purer clays and kaolins are often deficient in it. The property is tested in the laboratory by molding briquettes of a special shape, which after drying out are pulled apart in a machine designed for the purpose. The strength of different kinds of clays, as determined in this manner, is given in the following table:

Tensile strength of clays.

	Pounds per sq. in.
Pure kaolins	5–20
Common brick clays	30–100
Pottery clays	100–500
Ball clays and other very plastic clays	200–500

It is a curious fact that though high binding power is usually associated with high plasticity, this is not invariably the case. Some of the plastic clays of New Jersey in use in the potteries are of comparatively low binding power. This can be explained, however, by the colloid theory as outlined in the preceding paragraph better than by any other theory as yet advanced. There are various kinds of particles which assume to varying degrees the soft, almost viscous, condition which leads both to plasticity and binding power. In order to illustrate what is meant let us suppose that an inert, non-plastic powder were to be mixed with egg albumen on the one hand and with a glue solution of equal viscosity on the other. Masses of some plasticity would be obtained in both cases, but on drying out the binding power

of the glue would be much higher than that of the albumin. The difference in such a case is attributable solely to the kind of cementing material which is present and its individual character. In addition to this it is undoubtedly true that the shape and size of the particles, and the proportional amount of plastic and non-plastic particles present have an important influence on these properties.

SLAKING.

The slaking of clays refers to the quality possessed by some of them of rapidly disintegrating and falling to powder when lumps are thrown into water. Such clays are usually less dense, that is to say bulk for bulk they are less heavy than those which do not possess this property. Clays that slake, if touched to the tongue will adhere to it, sometimes so strongly that it is painful to draw the tongue suddenly away. Both this effect and the slaking are caused by a vigorous indrawing of water into the porous structure of the particles. In more dense clays this porous structure is already "stuffed" sometimes with water and quite often with other substances both of organic and inorganic origin. The truth of this is readily shown by a very simple experiment. Glycerin is not absorbed into the clay structure rapidly enough to produce slaking; if, therefore, a lump of slaking clay be soaked in glycerin over night it can be transferred to water in which it will then be found to behave as does any non-slaking clay.

Clays that have been slaked and the powder molded into masses and air dried do not again disintegrate when wet, as the porous structure is then sufficiently saturated with water to decrease the action. The power to slake readily is often a great advantage, as it enables hard clay masses from the bank to be disintegrated by weathering and thus does away with the necessity for elaborate grinding processes.

AIR SHRINKAGE.

Air shrinkage is that which takes place during the air-drying of a clay mass and is caused by the evaporation of the water, both that which has been used in mixing and a portion of that which the clay contains. As has been explained, very plastic clays possess a greater number of the active hydrated particles with a porous structure, so that we should expect these clays to exhibit a higher shrinkage than lean clays, and this is actually found to be the case. Everyone is familiar with the way glue-like bodies shrink on drying. This shrinkage varies in different clays from 1 to as high as 10 per cent. We now begin to see why the skill of the potter is highly taxed even before his ware goes to the kiln. If he selects a clay which from its plasticity and binding power is all that could be desired, it is probable that its high air shrinkage will cause it to deform and check (crack) on drying out. Sometimes by very slow and careful drying the danger can be avoided, but usually

another leaner material, sometimes even sand itself is mixed in just such an amount as to reduce the shrinkage without too far lowering the other useful qualities.

FIRING QUALITIES.

Many difficulties must be overcome in order to obtain a clay mixture which will burn well in the kiln and produce the desired result with the utmost economy. Of course the selection of the right kind of kiln and the proper control of the fire is of paramount importance. Such questions can not be treated in an article of this nature and larger works on the subject must be consulted.

Fire shrinkage.—After a clay mass is thoroughly air-dried it undergoes a further shrinkage on heating as the water of combination already referred to is driven out and the particles softened by incipient fusion followed by vitrifaction, draw together and adhere. By incipient fusion is meant the point at which the particles become soft in the fire and by vitrifaction the point at which they fuse together. Common bricks and earthenware are baked only to this first point and retain an open and porous structure, the bond of incipient fusion being sufficient to form the clay into tough, stone-like materials. Paving bricks and many kinds of stoneware are vitrified.

Fusibility.—It is well known that if pure crystalline substances are heated they become gradually hotter without apparent softening until a certain critical thermometric point is reached at which the crystals suddenly melt and the mass assumes a liquid condition. If, on the other hand, a noncrystalline, amorphous substance like glass is heated, it begins very soon to soften and continues to grow continually more viscous until it finally flows. In other words, crystalline substances have sharp and definite melting points while amorphous substances have none at all, but soften gradually to the point of flow. As has already been mentioned, there is evidence to show that clays are mixtures of crystalline and amorphous particles in varying proportions, and it may now be further pointed out that, in the fire, clays behave just as we should expect such mixtures to do. If clays had a sharp melting point, owing to the difficulty of exact control of temperature, the potter would be in continual danger of melting his ware to formless lumps, while on the other hand he could obtain no vitrified bond unless the particles first softened to the point of incipient fusion. As a matter of fact in most clays the point of incipient fusion is lower by from 100° to 500° F., than the point of vitrifaction, and this point in its turn may be many hundred degrees below the point of deformation and flow. Common brick clays will usually fuse at 2,000° F., while many of the better grades of clays will stand 3,000° without viscosity or deformation, while fire clays go as high as 3,500° and even more. It will be apparent from what has been said that a clay which will stand a considerable increase in temperature above a given point without softening to the point of

deformation and flow will be—other things equal—the safest and easiest clay to burn.

We have now to consider briefly the elements which actually determine the fusibility of clay. Quartz is an oxid of silicon formed by the association of two atoms of oxygen, with one atom of the element silicon to form the oxid silica, which is expressed by chemists by the symbol SiO_2. Silicon is one of a group of elements which always form acid oxids, so called because if heated with the proper amount of certain alkaline or basic oxids like lime, which is an oxid of calcium (CaO), they will combine to form fusible slags which are neutral, showing neither an acid nor an alkaline character. Silica has a very high melting point, and lime an even higher one, so high in fact that it withstands the extreme temperatures of the electric arc. If, however, the two oxids be mixed together the fusing point is lowered. Thus in clays the point of fusion depends upon the amount of fluxing agents present, such as the basic substances, iron oxid, soda, potash, lime, and magnesia; and, although fineness of grain is also an element in determining fusibility, the point of fusion will usually fall with the percentage of these basic substances present. For this reason the common red brick clays which get their color from iron oxid are, as a rule, of low fusing point.

Color.—The color of a clay before it is burned is of little importance except in so far as it serves to indicate the presence of iron. In the kiln, however, except in perfectly white clays which burn white, color changes invariably take place. Many black clays stained by organic matter burn white, while others burn to reds, buffs and cream colors. Nothing of importance has ever been accomplished technically in causing a dark burning clay to burn white. It is known that an increase in the amount of lime will produce a paler burn if the color is due to iron, but, on the other hand, such an admixture has certain deleterious effects, such as lowering the fusing point unequally.

ABSORPTIVENESS.

The power that some clays have to rapidly absorb water and other substances, has already been discussed. This property is frequently made use of in the arts. In addition to this action certain unctuous varieties of clay which will not usually adhere to the tongue have the power of removing coloring matters from solutions by actually adhering to the fine particles of matter held in suspension and "sweeping" them away. These clays are known as fullers earth and are much used as clarifying and bleaching agents. They are usually of a grayish-green color very soft and greasy to the touch and if placed on the tongue they appear to melt away.

PURIFICATION AND TREATMENT OF CLAYS.

In ordinary brickmaking the clays are not usually given much preliminary treatment, as it would increase the cost of manufacture too

much. In the manufacture of high-grade and art pottery, however, it is often worth while to go to any length in the effort to obtain an even standard of excellence. By means of grinding, washing, and sifting the clays are reduced to the even and uniform texture which is absolutely essential to the production of high-class work. In addition to these processes it has been found that by allowing the clay masses which have been worked up with water to the consistency of a pasty dough to remain quietly in this condition for long periods, months or more, the binding power and plasticity increase. This is called tempering or ripening the clay and has been ascribed by some observers to bacterial action. It will readily be seen, however, that according to the colloid theory, as already outlined, the effect gained is caused by the gradual softening of the active particles under the influence of water.

A number of researches have been carried on during the last few years in an attempt to find cheap and economical methods for increasing the useful properties of clays. One experimenter, having occasion in 1901 to seek a clay of the highest possible binding power, soon learned that the material suited to his purpose could only be obtained in Europe, and more particularly in Germany. This experimenter immediately began to seek for a method of treatment for local clays which would develop the useful qualities necessary for his purpose. After some experimentation it was found that by a preliminary soaking in a 2 per cent solution of tannic acid, or the ordinary catechu of commerce, the binding power and plasticity of most clays were very much increased while the air shrinkage was diminished. Even infusions of dried leaves and straw were found to produce the effect to some extent. The process was called the "Egyptianizing of clay" on the somewhat fanciful theory that the ancient Egyptians used straw in brickmaking more on account of the strength given by the infusion than by the fiber.

This subject was investigated in a general way in the Division of Tests, and it was found that many substances have the effect of producing increased binding power and apparently increased plasticity in some clays. This is shown by the tensile strength tests given in the following table, made on a buff-baking brick clay. Each result is the average of 30 to 40 briquettes, from 10 to 12 having been made by each of three operators.

Average tensile strengths of treated clays.

	Pounds per square inch.
Water	65
Two per cent solutions of—	
Tannic acid	153
Dilute ammonia	147
Alum solution	98
Iron alum solution	118
Dilute hydrochloric acid	63
Dilute caustic alkali (KOH)	80

Many other substances were also tried, but as the effects were not in all cases decisive they have not been included here. It will be observed that among the solutions tried, tannic acid, ammonia, and the alums were the most active in increasing the tensile strength.

On first thought these results are by no means easy to interpret. Tannic acid and the alums are astringent and of decidedly acid reaction in their water solutions, whereas ammonia is decidedly alkaline in reaction and detergent in its action. On the other hand, if alum is added to clay suspended in water to form a "slip," it will have a flocculating or coagulating effect upon the colloid particles, causing them to settle rapidly. Tannic acid and ammonia appear, in most cases, to have a deflocculating effect, and some clays, suspended in dilute ammonia, show no indication of settling after the lapse of several months. It is known that the colloid structure of clays is selective in its action, that is to say, tannic acid and ammonia will be taken out of solution and retained in the porous particles of a clay. This absorption then probably affects to some extent the flotation of the particles. In the writer's opinion the action of reagents in increasing the binding power of clays is twofold: (1) Deflocculation produces a better distribution of the colloid particles or a so-called "puddling" of the clay; (2) the colloids present are modified and developed, if not actually formed, by the reactions which take place. A further discussion of this interesting subject is of too technical a nature to be given here, but the question will be more fully treated in other publications.

USE OF CLAYS.

The various uses of clays is shown by the following list originally compiled for Mineral Resources, United States, 1891, published by the U. S. Geological Survey:[1]

Domestic.—Porcelain, white earthenware, stoneware, yellow ware, and Rockingham ware for table service and cooking; majolica stoves; polishing brick, bath brick, fire kindlers.

Structural.—Brick, common, front, pressed, ornamental, hollow, glazed, adobe, terra cotta; roofing tile; glazed and encaustic tile; drain tile; paving brick; chimney flues; chimney pots; doorknobs; fireproofing; terra cotta lumber; copings; fence posts.

Hygienic.—Urinals, closet bowls, sinks, washtubs, bath tubs, pitchers, sewer pipe, ventilating flues, foundation blocks, vitrified bricks.

Decorative.—Ornamental pottery, terra cotta, majolica, garden furniture, tombstones.

Minor uses.—Food adulterant; paint fillers; paper filling; electric insulators; pumps; fulling cloth; scouring soap; packing for horses' feet; chemical apparatus; condensing worms; ink bottles; ultramarine manufacture; emery wheels; playing marbles; battery cups; pins, stilts, and spurs for potter's use; shuttle

[1] Clays of the United States East of the Mississippi River, by Heinrich Ries, U. S. Geol. Sur. Professional Paper No. 11.

eyes and thread guides; smoking pipes; umbrella stands; pedestals; filter tubes; caster wheels; pump wheels.

Refractory wares.—Crucibles and other assaying apparatus; gas retorts; fire bricks; glass pots; blocks for tank furnaces; saggers; stove and furnace bricks; blocks for fire boxes; tuyeres; cupola bricks.

Engineering works.—Puddle; Portland cement; railroad ballast; water conduits; turbine wheels.

THE TESTING AND EXAMINATION OF CLAYS.

Although the testing of clays does not properly fall within the scope of a paper of this nature a few words on the subject will probably be of interest. There is a very widespread impression that the nature and uses of a clay body will be revealed by a chemical analysis alone. It is true that combined with other data the results of complete chemical analysis are always of value, but the fact remains that clays of widely different properties will have almost identical chemical composition and vice versa. This is illustrated by the analysis of two samples, one a fat ball clay from Florida, and the other a rather lean fire clay from Kentucky.

Chemical analyses of two clays.

Constituents.	Florida ball clay.	Kentucky fire clay.
	Per cent.	*Per cent.*
Silica	47.01	47.70
Alumina	38.50	38.47
Iron oxid	.35	Trace.
Lime	0.08	0.112
Magnesia	0.15	0.11
Potash	0.83	0.57
Soda		
Combined water	13.78	13.03

In addition to the usual chemical analysis, it is customary to examine clays by methods of so-called *rational* analysis, in which the effort is made to distinguish between the silica which is combined with alumina as clay substance and that which is free as quartz or sand. While somewhat inaccurate such analyses are of undoubted value.

The amount of water required to be mixed with air-dried clays to bring them to just the proper consistency for molding into forms varies greatly in different clays. It is evident from what has been said in an earlier paragraph that the smaller the amount of water present the less the danger from air shrinkage and the greater the economy of working, especially when artificial heat is used in the drying process. In a thorough report on the useful qualities of a clay this property should always be tested. The physical characteristics which it is necessary to test in a complete examination of clay are best shown by the following laboratory form:

Physical characteristics of clays.

No.	Kind of clay.	Water required	Tensile strength.		Air shrinkage.	Fire shrinkage.	Temperature required for—			Color when burned.	Remarks.
			Average.	Maximum.			Incipient fusion.	Vitrifaction.	Viscosity.		
		Per ct.			*Per c.*	*Per c.*	°*C.*	°*C.*	°*C.*		
722	Brick	17.4	65	72	2	2	1140	1430	1600	Buff	
925	Surface	28.0	35	40	3	------	1000	--------	--------	--------	Melted at 1400° to a slag.
926	Blue	19.0	130	145	7	8	1140	1430	1600	Coffee	
930	Fire	18.5	110	115	3	2	2500	--------	--------	Cream whites	

When a sample of clay is sent to the laboratory to be tested the following rules should be observed by the shipper. The sample should not weigh less than 30 pounds in its air-dry condition, and it should represent as nearly as is possible the average quality of the deposit from which it is taken. The laboratory should be put in full possession of such information as is available both as to the extent of the deposit and the purpose for which the report is desired. In some cases it happens that the interest in a clay is centered in its ability to hold water, for use in building canals or irrigation ditches. Clays vary as much in their permeability as in other qualities, but it is manifestly a waste of the chemist's time to investigate the firing qualities of a clay when simple percolation tests are all that is necessary.

ALLERTON S. CUSHMAN,
Chemist, Division of Tests.

Approved:
JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., *July 25, 1904.*

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